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1 white man, at $1.25 per day, 48 days	$60
5 colored men, at 75 cents per day, 48 days	180
2 teams, with wagons, at $2 each per day, 48 days	192
Total labor	$432
Chemicals	70
Wear and tear on sprayers	20
Grand total	$522

It will be seen from the foregoing that the cost of treating one tree four times (estimating 16,000 trees) was 3 cents and 2 mills, the cost of treating one tree once was 8 mills, and the cost of treating one acre (estimating 203 acres) was $2.56.

It is undoubtedly true that the four treatments were more than were necessary, and that two sprayings well done would be all that could be desired, as shown by the experimental plats. In other words, had the facts brought out by the experiment been known at the beginning, the cost of spraying the orchard could have been reduced one-half.

It is important to notice that the principal cost was the labor in applying the mixture, the men and teams costing more than four-fifths of the total amount. The cost of the fungicide and apparatus was a relatively small matter. This suggests that future experiments should be directed toward improving the means of distributing the fungicide, and thereby reducing the amount of labor required.

DESCRIPTION OF PLATES.

PLATE XXXII.—Bartlett pear tree sprayed with Bordeaux mixture.
PLATE XXXIII.—Bartlett pear tree untreated and defoliated by leaf-blight.

EXPERIMENTS WITH FUNGICIDES TO PREVENT LEAF-BLIGHT OF NURSERY STOCK.

By D. G. FAIRCHILD.

The following paper gives details of experiments carried on at Geneva, N. Y., to prevent leaf-blight of pear and other seedlings. An abstract of the work has already been published,* but in this paper there will be given in detail the various formulæ used, with notes upon chemical reactions and upon the effects of the different substances employed.

EXPERIMENTS WITH PEAR SEEDLINGS.

The experiment with pear seedlings was carried on in coöperation with Prof. S. A. Beach, botanist of the New York State Experiment Station. I wish here to express my thanks to him for his careful attention to the planting and cultivation of the seedlings, for his assistance in their treatment, and for his valuable aid in taking notes upon the results.

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* Report of Sec. of Agr. for 1892, pp. 224–229.

The experimental block was situated only a few feet south of the main nursery experiment described in a previous paper.* All rows ran north and south, at right angles to the rows of the main experiment. Each row was 20 feet long and at first consisted of about 250 small seedlings, but these were thinned out until only from 130 to 150 remained.

The seed for the experiment was received, through the kindness of Mr. S. D. Willard, from Vilmorin, Andrieux & Co., of Paris, in February, 1891. It was imported mixed with moist sand and kept in the ice house until April 20, 1892, when it was sown in shallow furrows, 4 inches wide by 2 inches deep, and covered with earth. Over the earth a thin layer of muck was spread.

The fall previous the ground had been sown to rye, which was plowed under in the spring, before planting the seeds. The land had been occupied by potatoes the year before, but no fertilizers had been applied to it. Hence the soil was not in the highest state of fertility, and it is not surprising that in a part of the field only a feeble growth was made by the seedlings. The usual methods of cultivation were employed.

The arrangement of the rows was somewhat irregular, but this was brought about in the attempt to separate all rows receiving like preparations by as much ground as possible. This method of treating duplicate rows has many advantages, and in fact should be considered as essential to the settlement of problems like the one here involved.

A spraying apparatus of my own contrivance was employed, consisting of a small Johnson hand force-pump fastened into a papier mâché pail by means of a thumbscrew. When many mixtures are to be employed this apparatus has several advantages over the knapsack pump, the principal one being the ease with which it can be cleaned. With several feet of hose, rows of considerable length can be very effectually sprayed. The Vermorel nozzle with a lance was employed.

In spraying care was taken that every leaf should be touched. The periods elapsing between the treatments were not long enough, it is believed, to allow the best mixtures to be washed off. In one or two cases it was found that the untreated adjacent rows had received occasional sprayings and it may be possible that an imperceptible mist was blown upon the control rows oftener than was observable, these being only 3 feet apart. It is believed, however, that this treatment of controls was so slight as not to vitiate the results in any way. The use of screens, made of light cloth or paper, to protect the control rows during treatment, would obviate any such difficulty.

The writer wishes to express his thanks to Messrs. W. T. Swingle and P. H. Dorsett, who assisted him very materially by suggestions and advice in the preparation of the fungicides. The preparations described below were, so far as my knowledge goes, first prepared by the parties above named. Those not mentioned were of my own invention or had been previously employed by others. Nos. 2, 18, 19, 20, 21, and 22 were first prepared by Mr. Galloway and Mr. Swingle in experiments with wheat rust at Garrett Park, Md.

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* Jour. of Mycol., vol. VII, pp. 240–264.

As it seemed advisable to adopt some arbitrary standard with which a comparison of the different substances could be made, it was decided to take as a standard the proportion of one part by weight of the metal forming the base of the salt to 1,000 parts of water. In the copper preparations it is 1:1,000; in the iron and zinc compounds, 2:1,000. It must not be supposed, however, that these are in all cases chemically accurate, since the substances used were not chemically pure and the water was not distilled. The same conditions prevailing, however, in each preparation it is thought that the comparative strengths are the same. One gallon of water was calculated to weigh 3,783 grams, and 3.78 grams of copper or 7.56 grams of zinc or iron, generally in the form of a sulphate, were used in the preparation of the mixtures. The proportion of the atomic to molecular weight gave the required weight of the salt to be used. In the preparation of the fungicides another point was kept constantly in view, viz, that no substance not in the finest possible state of division should be sprayed upon the seedlings. In order to secure the chemicals in this condition it was necessary to prepare precipitates and apply them before they became dry.

It has been found that dry, insoluble copper compounds, like cupric carbonate, when mixed with water do not split up into their smallest components, and hence do not adhere to the foliage as tenaciously as freshly prepared precipitates of the same substances. As will be inferred from the above, the preparation of each chemical necessitated the use of two or more ingredients, one the salt of the metal and the other an alkaline salt. With four exceptions the substances were all insoluble compounds, and by numerous titrations the optimum proportion of the salt containing the metal to that containing the alkali was established. By optimum is here meant that proportion which gave the lightest and most flocculent precipitate. Of two precipitates of the same salt, other things being equal, that one which remains longest suspended in the water is, according to the writer's idea, best suited for a fungicide. A rapidly settling fungicide is to be avoided if possible.

A test with potassium ferrocyanide was made to ascertain if any cupric sulphate remained in solution. As explained subsequently, there was present in all the mixtures a soluble salt, resulting from the combination of the alkali with the acid of the metal salt. This is indicated by the notes given after the name of the fungicide.

The plan of the experiment was made as simple as possible. Twenty-five substances mixed in water were applied to 50 rows of seedlings, that is, each substance was applied to 2 rows. These rows did not stand side by side, but were separated by at least 60 feet. On each side of every treated row stood an untreated one to serve for comparison. Thus 102 rows were planted, 51 standing south of a 5-foot alley, and 51 north. Every other row in the south block was treated, beginning with the second row. Each treatment made on the south block was duplicated upon the north block, rows treated with the same substances being placed as far apart as possible, in no case nearer than 60 feet. All rows were planted with seed from the same lot and as nearly as possible in the same manner. They were given precisely the same normal nursery treatment, being thinned out, hoed, and cultivated as nearly as possible on the same days. The seeds germinated normally and produced "stands" of uniform vigor, and not until the influence of the soil began to make itself felt was there the slightest difference noticeable between any of the rows. The unevenness of the soil, however, soon disturbed this uniformity and proved a more potent factor than the disease, but owing to the arrangement of the rows in duplicate it in no way disturbed the experiment.

The twenty-five chemicals which it was designed to test were all carefully weighed out, and concentrated solutions were prepared during the winter of 1891–'92 in the Department and shipped to Geneva ready to be diluted and applied to the seedlings with a sprayer.

The test of the preparations must be considered as wholly preliminary and designed to form a basis for further investigations. Hence the fact that a large number of the substances failed to prevent the disease by no means signifies that they may not yet prove to be true fungicides when of a suitable strength. According to the writer's notion, there is one requisite for, and two main limitations to, the preparation of a valuable fungicide. The requisite is that the preparation be a true fungicide and prevent infection from the disease. The limitations are, (1) that the expense of the material and its application, including the element of danger, shall not be greater than the benefit will warrant; and (2) that the effect upon the plant to be protected shall not be injurious. Any substance which fulfils the above requirements and does not overstep the limitations will prove a valuable fungicide.

Before it is possible to thoroughly test preparations with regard to the limitations above mentioned, it is necessary to gain some idea as to what mixtures are likely to be available for use and to eliminate those which from a combination of injurious and nonfungicidal properties are manifestly unworthy of further trials. In the summary the various mixtures have been grouped into three classes, clearly showing which are likely to be valuable.

In designating the different mixtures the exact chemical name of the supposed active salt has been used wherever the composition of such is known, otherwise the less specific title has been given.

The following is a list of the substances used, with the formulæ for their preparation and a statement of their effect upon the seedlings. The term "mixture" is here used in its broadest sense, to include the whole product of the chemical reaction which takes place when two or more salts in solution are added together. In the majority of cases the mixture was a solution of sodium or potassium sulphate, with an insoluble metallic salt, either copper, zinc, or iron. The remarks upon the effect of the different preparations are designed as an aid to those who may wish to make further trials with them.

In order to get more definite ideas as to the preventive effects of the various preparations, six grades were established. These were arbitrarily chosen as follows: Grade 1, in which were placed all rows in which the injury to the foliage amounted to from 1 to 15 per cent; grade 2, from 16 to 30 per cent; grade 3, from 31 to 50 per cent; grade 4, from 51 to 70 per cent; grade 5, from 71 to 85 per cent; grade 6, from 86 to 100 per cent. The grade in which each row was placed was decided on after a careful examination and comparison by Prof. Beach and myself. It is believed that the comparative injury done by the disease upon the different rows is for all practical purposes shown as faithfully in this way as it could have been if every seedling had been counted and its condition tabulated. The grading was done twice, once on September 2 and again on October 13.

Under the description of each preparation there is given a comparison of each treated row with the two adjacent untreated ones. In order to make a fair comparison the average of the two untreated rows was taken, and with this the treated row was compared.

Mixtures and solutions tested.—In the twenty-five mixtures described below, where not otherwise stated the ingredients were each dissolved separately in 1 quart of water and thoroughly mixed together. The mixture was then made up to 1 gallon, and 1 quart of this was applied to each row of 130–150 seedlings on each of the following dates: (1) June 3–5, (2) June 14 and 15, (3) July 6, (4) July 20, (5) August 1, (6) August 15.

NO. 1.—BASIC CUPRIC ACETATE MIXTURE.

(Rows 1 and 1^1.)

11.90 grams of copper acetate (basic refined powder).

Wet up to a thick paste and allowed to stand 24 hours or more before mixing in 1 gallon of water.

Chemical notes.—This refined powder is evidently a tribasic acetate, and, according to Watts' Dictionary of Chemistry, new edition, vol. I, p. 10, has the formula $2CuO, CuA'_2 2aq. = 3CuO, Ac_2O, Ac_2O2aq. = 2(HO, CuA')Cu(OH)_2$. The basic acetate has been used previously (see Div. of Veg. Path. Bull. No. 3, pp. 11 and 65. Also Beucker, Georges. <Prog. Agr. et Vit., Dec. 7, 1890, pp. 510–516.)

Remarks.—This mixture is easier to prepare, covers the foliage as well, and adheres as well as ammoniacal solution. It proved more effective in retarding the progress of the disease and was not injurious. The treated rows were ½ and 2 grades better than adjacent untreated rows on September 2, and 1½ and 1 on October 13. (The number first mentioned, denoting superiority, refers to the original row (1); the second to the duplicate row (1^1).)

NO. 2.—COPPER BORATE MIXTURE.

(Rows 2 and 2^1.)

14.90 grams cupric sulphate ($CuSO_4$, $5H_2O$).
16.39 grams sodium borate (borax) ($Na_2B_4O_7$, $10H_2O$).
1 gallon of water.

Chemical notes.—The borate has probably the formula $(Cu_2H)BO_3 + \frac{1}{2}$ aq., which on being decomposed by the water becomes $CuBO_2$. $3CuHO + \frac{1}{2}$ aq. (see Watts' Dictionary of Chemistry, old ed., 1863, p. 643). The substance was used as a dried precipitate by Lodeman,* but it was first proposed in its present form by W. T. Swingle and used for rust of wheat.† The reaction would be represented by the following formula: $CuSO_4, 5H_2O + Na_2B_4O_7, 10\,H_2O = CuB_4O_7 + Na_2SO_4 + 15H_2O$. It is therefore sprayed upon the plant in the form of a copper borate and a sodium sulphate.

Remarks.—This mixture is more difficult to prepare and does not cover the foliage as well, but adheres better than ammoniacal solution. It proved more effective in retarding the disease and was not injurious. The treated rows were 1 and 2 grades better than adjacent untreated rows on September 2, and 2½ and 1 on October 13. It is one of the most promising mixtures as regards efficacy, and might be tried stronger.

NO. 3.—COPPER BASIC CARBONATE MIXTURE.

(Rows 3 and 3^1.)

14.90 grams cupric sulphate ($CuSO_4$, $5H_2O$).
14.90 grams sodium carbonate ($Na_2CO_3 + 10H_2O$).
1 gallon of water.

Chemical notes.—This precipitate when first formed probably has the following formula: $CuCO_3$, CuO_2H_2, H_2O, but it rapidly becomes $CuCO_3$, CuO_2H_2 (see Watts' Dictionary 1888, p. 698). It is the mixture previously known as the "Masson" mixture and is identical with the first compound formed in the preparation of modified eau céleste. The reaction is expressed as follows: $CuSO_4, 5H_2O + Na_2CO_3, 10H_2O = CuCO_3 + Na_2SO_4 + 15H_2O$. The preparation, therefore, reaches the plant in the form of a copper carbonate and a sodium sulphate combined.

Remarks.—This mixture is more difficult to prepare than the ammoniacal solution, but it covers the foliage and adheres about as well. It proved more effective in retarding the progress of the disease and was not injurious. The treated rows were 1 and 2 grades better than adjacent untreated rows on September 2, and 3 and 2 on October 13. It is one of the most promising of the new fungicides as regards efficacy and should be tried stronger.

NO. 4.—AMMONIACAL COPPER CARBONATE SOLUTION.

(Rows 4 and 4^1.)

7.03 grams cupric basic carbonate (copper carbonate) ($2\,CuO, CO_2(OH)_2$).
50 c. c. of water.
150 c. c. of aqua ammonia, 26 per cent (stronger water of ammonia) (NH_4HO.)
1 gallon of water.

The carbonate is wet up in the small quantity of water to a thin paste, and after a few minutes the ammonia is added and the solution thus formed made up to 1 gallon.

Chemical notes.—The reactions for this fungicide, which is the ammoniacal solution as ordinarily used, with the addition of more ammonia than common, have been published by F. D. Chester in the Journal of Mycology, vol. VI, p. 23. A large quantity of ammonia was found necessary to a *complete* solution of the carbonate, but it was highly injurious.

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* Lodeman, E. G. N. Y. Cornell Agr. Exp. Sta., Bull. No. 35, pp. 327, 331.

† Jour. of Mycol., vol. VII, No. 3, May, 1893, p. 201.

Remarks.—This solution was taken as the standard with which the others are compared, although it injured the leaves and necessitated a dilution to 2 gallons. The excess of ammonia necessary to dissolve the carbonate was probably the cause of the injury. The grading was not upon the injury, but only as regards the disease. The manner in which this solution spreads and adheres is well known and forms a basis for comparison. The treated rows were graded -1 and 1, or no better than adjacent untreated rows, on September 2 and 5, and 1 better on October 13.

No. 5.—CUPRIC FERROCYANIDE MIXTURE.

(Rows 5 and 5^1.)

14.90 grams cupric sulphate ($CuSO_4$, $5H_2O$).
22.35 grams potassium ferrocyanide (yellow prussiate of potash) K_4FeCy_6, $3H_2O$.
1 gallon of water.

Chemical notes.—A well-defined chemical compound, with the formula $Cu_2Fe_2Cy_6$, with possibly CuK ferrocyanide present (see Watts' Dictionary, *l. c.*, 1889, p. 325). The reactions, however, were not obtainable. It is used ordinarily as a delicate test for the presence of Cu in solution. According to observations of Miss E. A. Southworth, spores of *Cladosporium fulvum* grew luxuriantly in drops of water containing this precipitate. The normal reaction would be as follows: $CuSO_4,5H_2O+K_4FeCy_6, 3H_2O=CuFeCy_6+K_4SO_4+8H_2O$. This would indicate that the substance sprayed upon the plants was a combination of copper ferrocyanide and potassium sulphate.

Remarks.—This fungicide is more difficult to prepare than ammonical solution, but covers the foliage as well and adheres about as well. It proved scarcely more effective, but did not injure the foliage. The treated rows were 1 and 0 grades better than the adjacent untreated rows on September 2, and $1\frac{1}{2}$ and 0 on October 13. Further tests are necessary with a stronger mixture to settle the fungicidal value of this preparation

No. 6.—CUPRIC HYDRATE, BLACK, MIXTURE.

(Rows 6 and 6^1.)

14.90 grams cupric sulphate ($CuSO_4$, $5H_2O$).
14.90 grams potassium hydrate (KHO) (caustic potash).
1 gallon of water.

The cupric sulphate and the potassium hydrate in concentrated solutions were mixed and allowed to stand until the mixture became black. Then the whole was made up to 1 gallon.

Chemical notes.—According to Prescott and Johnson (Qualitative Chemical Analysis, 4th ed., 1891, pp. 86–87), the combination formed when $CuSO_4$ and KHO are allowed to stand in contact is represented by the formula $Cu_3O_2(OH)_2$ if the solutions are both concentrated and the KHO is added to saturation. The normal reaction of the two substances as given above will be $CuSO_45H_2O+2KHO=Cu(HO)_2+K_2SO_4+5H_2O$. In the substance sprayed upon the plant there is, therefore, a combination of copper hydroxide and potassium sulphate.

Remarks.—This mixture is more difficult to prepare and does not cover or adhere to the foliage so well as ammoniacal solution. It proved more effective in retarding the progress of the disease and did not injure the foliage. The treated rows were $\frac{1}{2}$ and 1 grades better than adjacent untreated rows on September 2, and $2\frac{1}{2}$ and 0 on October 13. It is a mixture possessing no particular merit, and is markedly inferior to the hydroxide Nos. 7 and 8, but should be tried stronger.

No. 7.—CUPRIC HYDROXIDE MIXTURE.

(Rows 7 and 7^1.)

14.90 grams cupric sulphate ($CuSO_4$, $5H_2O$).
29.80 grams potassium hydrate (KHO).
1 gallon of water.

Prepared in the same way as No. 6, but applied before turning to the hydrate.

Chemical notes.—The original intention was to have the formula as follows: 14.90 grams cupric sulphate, 7.45 grams potassic hydrate, and 1 gallon of water, but by a mistake the KHO was double the amount of cupric sulphate instead of being only one-half the amount. The original would have formed a basic sulphate, since KHO when added short of saturation to $CuSO_4, 5H_2O$ gives a basic sulphate (see Prescott and Johnson, *l. c.*, pp. 86-87). The chemical formula of the hydroxide would be $Cu(OH)_2$, and in addition to the hydroxide present in the mixture there would be potassium sulphate. The reaction is the same as for No. 6.

Remarks.—This mixture is scarcely more difficult to prepare, covers the foliage as well, and adheres about as well as ammoniacal solution. It proved markedly superior in retarding the progress of the disease, but injured the foliage slightly. The treated rows were 0 and 2 grades better than adjacent untreated rows on September 2, and 2 and 2 better on October 13. It is certainly worthy of further trial, and is markedly superior to the black hydrate No. 6.

No. 8.—CUPRIC HYDROXIDE MIXTURE.

(Rows 8 and 8^1.)

14.90 grams cupric sulphate ($CuSO_4, 5H_2O$).
26.82 grams potassium hydrate (KHO).
1 gallon of water.

Prepared exactly as No. 7.

Chemical notes.—This mixture, which was intended for the simple hydroxide, was, because of a mistake in using an increased amount of potassium hydrate instead of a diminished amount (26.83 grams instead of 8.27 grams), applied as a hydroxide, with a large excess of KHO. It differed from No. 6 only in not being allowed to stand and thus become a black hydrate and from No. 7 in having less KHO. The substances in the sprayed mixture were the same as in Nos. 6 and 7, and the reaction would be the same.

Remarks.—In ease of preparation and application and in adhesiveness this mixture is like No. 7. It proved superior to ammoniacal solution in retarding the disease, but injured the foliage slightly. The treated rows were 1½ and ½ grades better than the adjacent untreated rows on September 2, and 0 and 1½ on October 13. It is slightly inferior to No. 7, but superior to No. 6. It differs in composition in no essential way from No. 7, and the difference in result is probably not significant.

No. 9.—TRICUPRIC ORTHOPHOSPHATE.

(Rows 9 and 9^1.)

14.90 grams cupric sulphate ($CuSO_4, 5H_2O$).
26.07 grams sodium phosphate ($Na_2HPO_4, 12H_2O$).
1 gallon of water.

Chemical notes.—The pearly blue precipitate thus formed is in all probability the tricupric salt mentioned in Watts' Dictionary, 1866, p. 560, and having the formula $Cu_3 P_2O_8$. No excess of $CuSO_4$ was observable in the supernatant fluid. The mixture as sprayed upon the plants was composed of copper orthophosphate and sodium sulphate. The reaction can be expressed as follows: $CuSO_4, 5H_2O + Na_2HPO_4, 12H_2O = CuHPO_4 + Na_2SO_4 + 17H_2O$.

Remarks.—This mixture is more difficult to prepare, but covers the foliage better and adheres better than the ammoniacal solution. It proved to have more efficiency in retarding the progress of the disease and did not injure the foliage. The treated rows were 1½ and ½ grades better than adjacent untreated rows on September 2, and 2½ and 0 on October 13. It is a mixture worthy of further trial.

No. 10.—CUPRIC POLYSULPHIDE MIXTURE.

(Rows 10 and 10^1.)

14.90 grams cupric sulphate ($CuSO_4, 5H_2O$).
14.90 grams potassium sulphide (K_2S_3 and K_2S_5 with intermediate forms) (liver of sulphur).
1 gallon of water.

Chemical notes.—Necessarily a more or less variable compound from the fact that the liver of sulphur is a variable factor, being composed of tri and penta sulphides, with the intermediate forms. The most probable formula is $Cu_2S_2 + Cu_2S_3 + Cu_2S_4$, or possibly a mixture of Cu_2S and Cu_2S_5 (see Watts, *Ibid.*, 1864, p. 76). Cupric sulphate seems to be present in slight excess, and from the reaction it is evident that this is combined in the solution with potassium sulphate.

Remarks.—This fungicide is only slightly more difficult to prepare, covers the foliage about as well, and adheres better than the ammoniacal solution. It proved inferior to the ammoniacal solution in retarding the disease, and injured the foliage. The treated rows were 1 and 1 grades better than the adjacent untreated rows on September 2, and 1 and 0 on October 13. Although much was hoped for from this mixture when first prepared, the experiment has not shown it to possess any remarkable fungicidal value.

No. 11.—COPPER SUCRATE MIXTURE.

(Rows 11 and 11^1.)

14.90 grams cupric sulphate ($CuSO_4$, $5H_2O$).
14.90 grams cane sugar ($C_{12}H_{22}O_{11}$).
14.90 grams potassium hydrate (KHO).
1 gallon of water.

Cupric sulphate is dissolved in water and the cane sugar is added. The two are heated to boiling and then the potassium hydrate is added. All solutions are strongly concentrated.

Chemical notes.—This mixture proved troublesome to make, from the fact that the "sucrate" if heated too much after the addition of the potassium hydrate became bright red, turning to the red oxide. When properly prepared the mixture is a dark, livid green. The reactions are too complex to be written. Evidently little is known of the exact composition of this peculiar compound, which differs entirely from that formed in the cold. It is not the "copper saccharate" of various French authors.

Remarks.—This mixture is much more difficult to prepare than ammoniacal solution, does not cover foliage any better, and is more easily washed off. It proved less effective in retarding the disease and injured the foliage slightly. The treated rows were 0 and ½ grades better than adjacent untreated rows on September 2, and 1½ and 0 on October 13. It is so complex and difficult of preparation as not to warrant further trial.

No. 12.—COPPER SILICATE MIXTURE.

(Rows 12 and 12^1.)

14.90 grams cupric sulphate ($CuSO_4$, $5H_2O$).
44.70 grams sodium silicate (Na_4SiO_4 (?)) (Prescott and Johnson, *l. c.*, p. 215, water glass).
1 gallon of water.

Chemical notes.—According to the chemical catalogues, water glass is a pure sodium silicate. No cupric sulphate could be detected in the supernatant fluid. It is a compound of which nothing definite seems to be known. It is not mentioned by Watts. The chemical reaction would be $2CuSO_4, 5H_2O + Na_4SiO_4 = Cu_2SiO_4 + Na_4 (SO_4)_2, + 5H_2O$. According to this the compound sprayed upon the plants would be a mixture of copper silicate and sodium sulphate.

Remarks.—This mixture is slightly more difficult than ammoniacal solution to prepare, covers the foliage about as well, but does not adhere as well. It proved much less effective in retarding the progress of the disease, but was not injurious. The treated rows were 0 and 0 grades better than adjacent untreated rows on September 2, and ½ and ½ better on October 13. It merits further trial only in a more concentrated form.

No. 13.—CUPRIC SULPHATE, AMMONIA, AND SOAP MIXTURE (SOAP EAU CÉLESTE).

(Rows 13 and 13^1.)

14.90 grams cupric sulphate ($CuSO_4$, $5H_2O$).
0.75 c. c. aqua ammonia 26 per cent (NH_4HO).
44.70 grams palm soap.
1 gallon of water.

The cupric sulphate was dissolved in water and the ammonia added to it. The soap previously dissolved in warm water was then added and the whole mixture churned until a heavy foam was formed.

Chemical notes.—Palm soap was used as being the most available, but other kinds of soap answer the purpose perfectly. This mixture is remarkable in its property of spreading over the foliage. The waxy cuticle of the pear leaves in no way prevents a complete coating from being formed. It is of indefinite composition and too complex to be determined.

Remarks.—Although more difficult of preparation than ammoniacal solution, this covers the foliage and adheres to it in a manner unsurpassed by any mixture yet employed, to my knowledge. It proved much more effective in retarding the progress of the disease and was not in the least injurious. It was tested upon the foliage of bearing pear trees and showed remarkable efficacy in checking leaf-blight. It was also used upon plum and horse-chestnut seedlings without the least injurious effect. Upon grape foliage it proved somewhat injurious. The treated rows of pear seedlings were $1\frac{1}{2}$ and 1 grades better than adjacent untreated rows on September 2, and 2 and 2 better on October 13. It is the most promising of all the 25 preparations employed. It is believed that the subject of soap mixtures is worthy of more extended investigation than it has hitherto received.

No. 14.—CUPRIC OXYCHLORIDE MIXTURE (FORM A).

(Rows 14 and 14^1.)

14.90 grams cupric sulphate ($CuSO_4$, $5H_2O$).
29.80 grams chloride of lime ($CaOCl_2$)(?).
1 gallon of water.

Chemical notes.—A sooty black precipitate, often with a brownish tinge, formed best when both cupric sulphate and chloride of lime are in concentrated solution. The proportions of lime and sulphate are highly important. The addition of a small amount produces a green precipitate (No. 15), while the addition of a greater portion causes it to turn to a sooty black color on standing. Free chlorine seems to be given off in the reaction. No cupric sulphate was detectable in the supernatant fluid. I was not able to determine the composition of this compound and believe little is known of it further than that it is probably an oxychloride.

Remarks.—This mixture is more difficult to prepare and apply than ammoniacal solution, spreads as well, but does not adhere nearly as well. It proved less effective in retarding the progress of the disease and was very injurious to the foliage, scorching it severely and necessitating a dilution to 2 gallons. The treated rows were $\frac{1}{2}$ and $1\frac{1}{2}$ grades better than untreated adjacent rows on September 2, and 0 and $\frac{1}{2}$ better on October 13. It is a mixture with nothing to recommend it.

No. 15.—CUPRIC OXYCHLORIDE MIXTURE (FORM B, TRIBASIC)

(Rows 15 and 15^1.)

14.90 grams cupric sulphate ($CuSO_4$, $5H_2O$).
21.28 grams chloride of lime ($CaOCl_2$) (?).
2 gallons of water.

Chemical notes.—This form of the oxide, according to Prescott and Johnson (*l. c.*), is known in commerce as "Brunswick green," and is used as a pigment. No cupric sulphate was in excess in the supernatant fluid. In Watts' Dictionary, edition of 1889, p. 260, it is stated that Brunswick green has the formula $CuCl_2$, $3CuO$, $4H_2O$.

Remarks.—This mixture is identical in method of preparation with No. 14, and differs from it only in being slightly less injurious to the foliage. It was diluted 2 gallons. The treated rows were 1½ grades better than adjacent untreated rows on September 2, and 1 and 1 better on October 13. The commercially prepared Brunswick green may not possess the injurious qualities to so high a degree as the freshly prepared precipitate and is worthy of a trial.

NO. 16.—COPPER SULPHITE MIXTURE.

(Rows 16 and 16¹.)

14.90 grams cupric sulphate ($CuSO_4, 5H_2O$).
37.25 grams sodium hyposulphite ($Na_2S_2O_3$, $5H_2O$) (U. S. Dispen., 15th ed., p. 1330).
1 gallon of water.

Chemical notes.—Cupric sulphate is in excess in the supernatant fluid. The precipitate settles rapidly, is of a dirty greenish-yellow color, and the proportions of the ingredients have little to do with the rapidity of subsidence of the precipitate. I am uncertain as to its composition.

Remarks.—This mixture, although scarcely more difficult to prepare than ammoniacal solution, covers the foliage no better, adheres no better, and proved very injurious, even after being diluted to 2 gallons. It was, however, more effective in retarding the progress of the disease. The treated rows were 1½ and 1½ grades better than adjacent untreated rows on September 2, and 0 and 2 better on October 13. It is doubtful if the mixture can be modified so as to fit it for use.

NO. 17.—FERRIC CHLORIDE AND PHENOL MIXTURE.

(Rows 17 and 17¹.)

36.46 grams ferric chloride ($Fe_2Cl_3 + H_2O$).
36.46 grams phenol (C_6H_5OH) (U. S. Dispen., p. 48) (carbolic acid).
1 gallon of water.

Chemical notes.—This forms a tar-black solution, emitting fumes of carbolic acid. The phenol used was of commercial strength, not crystallized, and equals 20 per cent of the crystallized. The perchloride of iron used has a formula of Fe_2Cl_3, according to Watts, 1865, p. 377, but the amount of water was not obtainable.

Remarks.—This mixture is slightly more difficult of preparation than ammoniacal solution, but extremely disagreeable to apply and highly injurious to the foliage. Dilution to 2 gallons seems to reduce the injury materially. In retarding the progress of the disease it proved less effective than ammoniacal solution. The treated rows were 1½ and 1½ grades better than untreated adjacent rows on September 2, and 0 and ½ better on October 13. It is a mixture altogether too obnoxious to warrant further trial.

NO. 18.—FERROUS FERROCYANIDE MIXTURE.

(Rows 18 and 18¹.)

22.94 grams ferrous sulphate exsiccatus ($FeSO_4$, H_2O).
45.88 grams potassium ferrocyanide ($K_4 FeCy_6$, $3H_2O$).
1 gallon of water.

Chemical notes.—A light marine-blue precipitate, which becomes dark Prussian blue on exposure to the air. The formula is probably Fe_2FeCy_6, with potassium ferrocyanide present (Watts, 1865, p. 334). The chemical reaction would be $Fe_2SO_4, H_2O + K_4FeCy_6, 3H_2O = Fe_2FeCy_6 + K_4(SO_4)_2 + 4H_2O$. The ferrous ferrocyanide is therefore combined in the mixture with potassium sulphate.

Remarks.—This mixture is considerably more difficult of preparation than ammoniacal solution, but covers the foliage as well and adheres with remarkable tenacity, far surpassing ammoniacal solution in this respect. It proved less effective in retarding the progress of the disease and was slightly injurious. The treated rows were 1 and ½ grades better than the adjacent untreated rows on September 2, and 0 and 2 better on October 13. It is a mixture seemingly possessing little fungicidal value.

No. 19.—IRON BORATE MIXTURE.

(Rows 19 and 19^1.)

22.94 grams ferrous sulphate exsiccatus ($FeSO_4$, H_2O).
91.76 grams sodium borate (borax) ($Na_2B_4O_7$, $10H_2O$).
1 gallon of water.

Chemical notes.—A steel-gray precipitate, becoming brown or yellow on exposure. Probably a basic salt of uncertain chemical composition (see Watts' Dictionary of Chemistry, 1888, p. 530). The chemical reaction would be written $FeSO_4, H_2O + Na_2B_4O_7, 10H_2O = FeB_4O_7 + Na_2SO_4 + 11H_2O$. The sodium sulphate is in combination with iron borate in the mixture as sprayed on the plants.

Remarks.—This mixture is much more difficult of preparation, covers the foliage no more effectively, and adheres no more tenaciously than ammoniacal solution. It proved almost entirely ineffective in retarding the spread of the disease and was highly injurious, scorching the leaves in a few minutes after application. The treated rows were 0 and ½ grades better than adjacent untreated rows on September 2, and 0 and 0 better on October 13. It was the most injurious of any of the mixtures employed and has no good qualities to redeem it.

No. 20.—FERRIC HYDRATE MIXTURE.

(Rows 20 and 20^1.)

22.94 grams ferrous sulphate exsiccatus ($FeSO_4$, H_2O).
11.47 grams potassium hydrate (KHO).
1 gallon of water.

Chemical notes.—The precipitate is of a dirty green color, changing on exposure to a rich brown. The ferrous compound, $Fe(OH)_2$, which is formed on adding potassium hydrate to ferrous sulphate, becomes, on exposure to the air, the ferric compound, $Fe_2(OH)_6$ (see Watts). It is probable, however, that the green ferrous ferric compound was that first formed, as the air was not, of course, excluded from the mixture. The chemical reaction would be $FeSO_4, H_2O + 2KHO = Fe(HO)_2 + K_2SO_4 + H_2O$. The ferric hydrate and potassium sulphate are therefore in combination in the mixture.

Remarks.—This mixture is more difficult of preparation than ammoniacal solution, covers the foliage about as well, and adheres as well, but was slightly injurious. It proved much less effective in retarding the progress of the disease. The treated rows were 0 and ½ grades better than untreated adjacent rows on September 2, and 0 and 0 on October 13. It is doubtful if this mixture has any fungicidal effect whatever.

No. 21.—IRON SULPHIDE MIXTURE.

(Rows 21 and 21^1.)

22.94 grams ferrous sulphate exsiccatus ($FeSO_4$, H_2O).
91.76 grams potassium sulphide (liver of sulphur, hepar sulphur).
1 gallon of water.

Chemical notes.—This mixture is in the form of an inky black fluid, which, on exposure, deposits an orange-yellow precipitate. When the proportion of potassium sulphide to ferrous sulphide is as low as three to one there is formed a precipitate in the liquid which gradually sinks to the bottom. Baric chloride gives the reaction for sulphuric acid in the solution. It is probably a compound of complex composition, as it is not described by Watts; possibly a potassium-iron sulphide (see Watts, 1872, p. 1077).

Remarks.—This mixture is more difficult to prepare than ammoniacal solution, covers the foliage no better, and adheres little if any better. It proved almost wholly ineffective in retarding the progress of the disease and was evidently slightly injurious to the foliage, although diluted to 2 gallons after the first application. The treated rows were 0 and ½ grades better than adjacent untreated rows on September 2, and 0 and 0 on October 13. Its fungicidal properties, if any, are slight.

No. 22.—ZINC BORATE MIXTURE.

(Rows 22 and 22^1.)

33.36 grams zinc sulphate ($ZnSO_4$, $7H_2O$).
33.36 grams sodium borate (borax) ($Na_2B_4O_7$, $10H_2O$).
1 gallon of water.

Chemical notes.—A remarkably gelatinous precipitate of a milky white color. The above proportions are necessary, as a variation either way from equal parts gives a precipitate which settles very rapidly. It is a compound of very vague composition (see Watts' Dictionary, 1888, p. 530). The reaction would be written $ZnSO_4$, $7H_2O + Na_2B_4O_7$, $10H_2O = ZnB_4O_7 + Na_2SO_4 + 17H_2O$. A zinc borate and a sodium sulphate are in combination in the spraying mixture.

Remarks.—This mixture is much more difficult of preparation than ammoniacal solution, covers the foliage less completely, and adheres with about the same tenacity. It proved markedly inferior in retarding the progress of the disease and injured the foliage slightly. The treated rows were 1 and ½ grades better than adjacent untreated rows on September 2, and 0 and 0 better on October 13. A mixture with no qualities to recommend it for further trial.

No. 23.—ZINC FERROCYANIDE MIXTURE.

(Rows 23 and 23^1.)

33.36 grams zinc sulphate ($ZnSO_4$, $7H_2O$).
66.72 grams potassium ferrocyanide (yellow prussiate of potash).
1 gallon of water.

Chemical notes.—A yellowish white precipitate is formed by the reaction, settling very slowly. An increase of zinc sulphate causes a heavy precipitate to be formed, which sinks very rapidly. According to Watts' Dictionary, 1889, p. 337, the formula is Zn_2FeCy_6, $3H_2O$. The solution sprayed upon the plants contains in combination zinc ferrocyanide and potassium sulphate.

Remarks.—This mixture is much more difficult of preparation, covers the foliage no more effectively, and adheres with about the same tenacity as the ammoniacal solution. It proved wholly ineffective in retarding the progress of the disease and injured the foliage, necessitating a dilution to 2 gallons. The treated rows were 0 and 0 grades better than untreated adjacent rows on September 2, and 0 and 0 on October 13.

No. 24.—ZINC SILICATE MIXTURE.

(Rows 24 and 24^1.)

33.36 grams zinc sulphate ($ZnSO_4,7H_2O$).
58.38 grams sodium silicate (water glass).
1 gallon of water.

Chemical notes.—An opalescent fluid with a precipitate which sinks very slowly. It is a compound of which little seems to be known. Watts does not include it. The chemical reaction would be written $ZnSO_4$, $7H_2O + Na_2SiO_4 = ZnSiO_4 + Na_2SO_4 + 7H_2O$. The mixture therefore contains zinc silicate and sodium sulphate in combination.

Remarks.—This mixture is more difficult of preparation, does not cover the foliage any better, and is less adherent than ammoniacal solution. It proved wholly without effect in retarding the progress of the disease and injured the foliage slightly. The treated rows were 0 and 0 grades better than adjacent untreated rows on September 2, and 0 and 0 on October 13.

No. 25.—ZINC SULPHIDE MIXTURE.

(Rows 25 and 25^1.)

33.36 grams zinc sulphate ($ZnSO_4,7H_2O$).
66.60 grams potassium sulphide (liver of sulphur).
1 gallon of water.

Chemical notes.—A very fine greenish or yellowish white precipitate. Gives off odor of H_2S when potassium sulphide is added. The proportions were intended to be 1 to 2, but by a mistake 66.60 instead of 66.72, grams were used. Probably the compound is not clearly defined, as the liver of sulphur is a mixture of the trisulphides and pentasulphides, with intermediate forms, but without much doubt ZnS_5 is formed from the pentasulphide of potassium combining with the $ZnSO_4$.

Remarks.—This mixture is more difficult of preparation than ammoniacal solution and adheres to the foliage more tenaciously, but was slightly injurious and necessitated dilution to 2 gallons. It proved of scarcely any value in retarding the progress of the disease. The treated rows were 0 and 1½ grades better than adjacent untreated rows on September 2, and 0 and 0 better on October 13.

Summary.—While none of the above mixtures or solutions were really effective in preventing the leaf-blight, the retarding effect which several of them had upon the progress of the disease makes it seem probable that if their strength be increased they may prove valuable. The results of the year's experiments make possible the following classification, which will enable the investigator to choose for further experiment those mixtures worthy of trial:

(1) Mixtures which did not injure the foliage and retarded more or less the progress of the disease: Nos. 1. 2, 3, 5, 6, 9, 12, 13.

(2) Mixtures which injured the foliage, but retarded the progress of the disease: Nos. 4, 7, 8, 10, 11, 14, 15, 16, 17, 18, 22, 25.

(3) Mixtures which injured the foliage and did not retard the progress of the disease: Nos. 19, 20, 21, 23, 24.

As will be readily inferred, those mixtures under (3) are plainly excluded from further trial; those under (2) may possibly prove of value if sufficiently diluted, but since they only imperfectly retard the progress of the disease when strong, they are not likely to be effective when of sufficiently weak strength, while those under (1) are worthy of further trial in stronger proportions.

It should be remarked here, however, that these experiments were with pear seedlings only, and before making them applicable to other plants a trial will be necessary. This is plainly shown in the grape experiments with the same mixtures, in which many of the preparations that were not injurious to pear foliage proved injurious to the grape. The results of these experiments will appear elsewhere.

The writer is most forcibly impressed with the remarkable nature of Bordeaux mixture in this respect. Although the trials made by Smiths and Powell, of Syracuse, N. Y., with Bordeaux mixture upon seedlings were not satisfactory the present season, I am still of the opinion that had it been tried upon the experimental plat it would have shown itself superior to any of the other preparations employed. So far it seems to be the only preparation which gives to the foliage of treated plants an appearance of unusual health.

HORSE-CHESTNUT LEAF-BLIGHT.*

Horse-chestnut seedlings are subject to leaf-blight to such an extent that it has come to be looked upon by many nurserymen as something entirely normal to their growth—a natural ripening of the foliage. The disease first makes its appearance toward the latter part of June, and before the middle of August the leaves are generally entirely dead, often remaining attached to the seedlings until the middle of October or later. Although the damage done to the foliage of fully grown trees is not as serious in this northern climate as it is in the neighborhood of Washington, D. C., the young trees of two or three years' growth often have their foliage materially injured by the parasite. The principal growth of the horse chestnut being made very early, i. e., in the first six weeks, it is doubtful whether the loss to the plant is as great as in plants with a longer period of growth. The reserve material stored up must, however, be much less in defoliated stocks than in those maintaining healthy foliage throughout the season.

The experiments in the prevention of horse-chestnut leaf-blight were inaugurated in 1892, and only a preliminary report as to the effects of the fungicides is possible.

Two rows, comprising in all over one thousand seedlings, were under treatment. The seed was gathered from trees growing on the station grounds and planted in the fall of 1891 in shallow trenches. Nearly every seed germinated and an excellent "stand" was secured.

One row was divided into twenty-four sections, each containing twenty-five or more seedlings, and treated with the same mixtures as those described previously as being used on pear seedlings. Preparations Nos. 13, 14, 15, 17, 18, 19, 20, 21, 22, 23, 24, and 25 were used. Only alternate sections were treated, the intervening sections serving as controls. The dates of treatment were June 22, July 6 and 20, and August 1 and 15. At these dates the foliage of each section was thoroughly wetted with the preparation.

The disease first made its appearance the last week in June and spread very slowly over the experimental rows, injuring the foliage very irregularly. The sections, with two exceptions, seemed to be little benefited by the treatments. Preparations 14, 17, 18, 19, 21, 22, 24, and 25 injured the foliage to a greater or less degree. The injury manifested itself generally by a sickly yellow or brownish coloration of the foliage. On October 14 the only two preparations whose good effects were visible were Nos. 13 and 25. When every stock in these sections was placed in one of four grades as regards injury to the foliage the record stood as follows:

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* *Phyllosticta sphæropsoidea* E. & E.

Treatment.	Number of seedlings.	Number in grade 1.	Number in grade 2.	Number in grade 3.	Number in grade 4.	Average grade.
Mixture No. 13	31	9	17	4	1	1.9
Control on No. 13	25	2	12	3	8	2.6
Mixture No. 25	26	0	20	4	2	2.3
Control on No. 25	31	0	11	9	11	3.0

The beneficial effects of the treatments with mixture No. 13 were plainly evident, and of the twelve mixtures employed this is the only one promising good results. The second row was divided into six sections, sections 1 and 2 being treated five and six times, respectively, with ammoniacal solution, and sections 4 and 6 on the same dates with Bordeaux mixture. The dates of treatment and the formulæ for the mixtures are given on a previous page, and were the same as those for the budded stocks treated in 1892. Sections 3 and 6 were intended to serve as controls, but unfortunately, by mistake, section 6 received one treatment on June 16 with Bordeaux mixture. The beneficial effect of the Bordeaux mixture was evident, as the disease spread upon the untreated sections, but the ammoniacal solution was plainly injurious to the foliage, the leaves which were treated with this assuming a faded brownish hue. In October the difference between the untreated stocks and those sprayed with Bordeaux mixture was marked. The former had lost many of their leaves and had few perfect ones, while the latter were provided with almost perfect foliage. No marked difference between five and six treatments was observable. The preventive effect of ammoniacal solution, while apparent, was, in the sections treated five and six times, inferior to that of Bordeaux mixture.

On October 15 the earth was removed from the base, and the seedlings of sections 3, 4, and 5 were calipered at the collar. The following data were thus obtained:

	Average caliper in $\frac{1}{32}$ of an inch.
74 seedlings untreated	12.8
57 seedlings treated 5 times with Bordeaux mixture	12.6
75 seedlings treated 6 times with Bordeaux mixture	12.6

As is shown, no difference in diameter of treated and untreated seedlings was observable. It is hoped that another year's observations upon the stocks may be made to ascertain the effect of maintaining the foliage upon plants like the horse chestnut, which make their principal growth before the disease defoliates them. This preliminary experiment, however, certainly warrants the recommendation of Bordeaux mixture as a preventive of horse-chestnut leaf-blight.